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IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC. — I. CURCUMIN.

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Presented December 14, 1881.

The chemical study of curcumin, the yellow coloring matter of turmeric, dates from a paper * by A. Vogel, Sr., and Pelletier, published in 1815, although even before this turmeric-paper had been used as a test for alkalies, and its action with boric acid and various salts observed.† No analysis is given in this paper, and the low melting-point (40°) and description of the method of preparation show that the "yellow coloring-matter of turmeric" obtained by Vogel and Pelletier was principally composed of resin and turmeric oil; they proved, however, that it contained no nitrogen, and studied its action with alkalies, acids, and certain salts, especially acetate of lead.

In 1842 A. Vogel, Jr.,‡ analysed a similar but perhaps somewhat purer preparation, which, however, must have consisted in great part of the yellow resin contained in the root, as it also melted at 40°; it is not wonderful, therefore, that his analyses led to no formula.

Passing over a number of unimportant notices,§ we come next to a

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* Journal de Pharmacie, i. p. 289.

† Trommsdorff, Trommsdorff's Journal von Pharm., xvi. p. 96. Sementini, Bibliothèque Britannique, Jan. 1815.

‡ Journ. de Pharm. et de Chim., sér. 3, ii. p. 20.

§ Desfosses, Ann. Chim. Phys., xvi. p. 76; A. Vogel, Jr., Répert. Pharm., sér. 3, iii. p. 178; H. Rose, Pogg. Ann., cii. p. 545; Lepage, Archiv der Pharm., Ser. 2, xcvii. p. 240; Leube, Vierteljahrsschr. pr. Pharm., ix. 395; Alex. Müller, J. pr. Chem. lxxx. p. 119; Wittstein, Vierteljahrsschr. pr. Pharm., ix. p. 282; Schutzenberger, Paraf. Mul. Soc. Bull., 1861, p. 503; Ludwig, Archiv der Pharm., cvi. p. 169; Kraut, Zeitschr. anal. Chem., iv. p. 168.

paper by Schlumberger,* in which the action of a mixture of sulphuric and boric acids on crude curcumin is studied, and a description given of the product called by him rosocyanin, because it dissolved in alcohol with a fine red color, and was turned blue by alkalies. He also describes a resinous product of the action of boric acid on curcumin (pseudocurcumin).

Two years later, in 1868, Bolley, Suida, and Lange † examined the turmeric oil, and published a new analysis of a purer curcumin (melting-point 120°); but it was not till 1870 that curcumin was obtained essentially pure. In this year Daube,‡ Ivanow-Gajewsky,§ and Kachler ‖ published independent papers on the subject, of which Ivanow-Gajewsky's is entitled to the precedence, as the number of the Berlin Berichte which contained Daube's original paper gave a notice in the Correspondence of the reading of Gajewsky's paper before the Russian Chemical Society a month earlier. In addition to an analysis of the turmeric oil, he assigns, as the simplest possible, the formula C_4H_4O to curcumin, which after crystallization from ether or benzin melted at 172°. Daube, on the other hand, after extracting his curcumin with benzol, and purifying it by conversion into the lead salt, obtained the melting-point 165°, and the formula $C_{10}H_{10}O_3$. He also found that it was decolorized by sodium amalgam and alcohol, and converted into oxalic acid by dilute nitric acid.

Kachler, who did not succeed in crystallizing his curcumin, although both Ivanow-Gajewsky and Daube got crystals, obtained the same formula as the former, that is, C_4H_4O, or some multiple of it. He also studied the action of sodium amalgam upon it, and that of hot zinc dust, but with no very definite results in either case; whereas by fusing curcumin with potassic hydrate, he obtained protocatechuic acid. From the turmeric oil he obtained essentially the same analytical results as Ivanow-Gajewsky.

In 1872 Ivanow-Gajewsky published a second paper ¶ on turmeric, containing another method for extracting curcumin, which, however, gave it a melting-point of 140°, and an analysis of the lead salt supporting his formula $C_{16}H_{16}O_4$ ($= (C_4H_4O)_4$). Moreover he confirmed the results of Kachler with fusing potassic hydrate (protocatechuic acid) and zinc dust, and states that the oil obtained with the latter is identical with turmeric oil, of which a new analysis is given, and its oxidation (yielding valeric and caproic acids) and action with phosphoric pentachloride studied. He also prepared and analysed rosocyanin, but was unable to find a satisfactory formula for it.

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* Bull. Soc. Chim. sér. 2, v. p. 194.

† J. pr. Chem., ciii. p. 474.

‡ Ber. d. ch. G., 1870, p. 609.

§ Ibid., 1870, p. 624.

‖ Ibid., 1870, p. 713.

¶ Ber. d. ch. G., 1872, p. 1103.

Finally, in 1873, he published the last paper [*] we have been able to find on this subject, in which he states that curcumin yields on oxidation with potassic dichromate terephthalic acid, and that rosocyanin contains no boron, and, fused with potassic hydrate, yields paraoxybenzoic acid.

In brief, the following facts had been established in regard to curcumin at the time that we began our research upon it: — Its formula was either $C_{10}H_{10}O_3$ or $C_{16}H_{16}O_4$; the highest melting-point observed was 172°; with alkalies it formed reddish-brown salts; with boric and sulphuric acids rosocyanin; it was susceptible of reduction, and gave an oil with zinc dust; by oxidation it yielded oxalic acid or terephthalic acid, and by fusion with caustic potash protocatechuic acid.

Accordingly we first turned our attention to the determination of its formula.

Extraction and Purification of Curcumin.

After several experiments we have adopted the following method as the best and most convenient: — The turmeric oil is first removed from the ground root by treatment with ligroine; [†] then the curcumin, mixed with a large quantity of resin, is extracted with ether, and finally purified by crystallization from alcohol.

The turmeric used by us has been principally Bengal turmeric, bought of Messrs E. and F. King, of Boston; we have, however, also extracted enough of the Madras turmeric, the only other brand occurring in the Boston market, to assure ourselves of the identity of the curcumin obtained from both.

For a full description and history of turmeric, which consists of the root-stocks of the *Curcuma longa*, a plant of the ginger family, growing in India and other parts of the East, we would refer to Flückiger and Hanbury's Pharmacographia, [‡] and to a full botanical article recently published by A. Meyer [§] in the Archiv der Pharmacie.

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[*] Ber. d. ch. G., 1873, p. 196.

[†] In our first experiments we followed Ivanow-Gajewsky, and used carbonic disulphide for this purpose; but we have found that ligroine is not only much cheaper and more agreeable to work with, but yields a purer oil.

[‡] Macmillan and Co., London, 1879.

[§] Arch. Pharm. Ser. 3, xviii. p. 401.

The extracter was of the form recently described by Scheibler,* as this was the only one of which we have found a description adapted to the thorough extraction of large quantities of material; those forms in which the drug is not kept covered with the extracting liquid being apt to leave the edges partially unacted on. The only modification of Scheibler's apparatus made by us consisted in substituting a cylindrical tin vessel capable of holding 10 kil. of ground turmeric for the smaller glass vessel used by him. With a cooler 78 cm. long, the inner tube of which was a flattened U, also made of tin, the thorough extraction of the 10 kil. of turmeric could be accomplished in little more than a fortnight. The solvent was removed, after it had ceased to act, by forcing out as much as possible of it by air pressure, and then distilling off the rest by filling with steam a jacket which surrounded the vessel containing the turmeric.

The ligroine extract yielded on evaporation a dark yellow oil, amounting on the average to eleven per cent of the weight of the root. The investigation of this substance will be described in a later paper.

The ether extract, a reddish-brown mass, varying in consistency from semi-liquid to solid according to the period of the extraction at which it was obtained, was treated with successive small quantities of cold alcohol, which dissolved the viscous impurities more easily than the curcumin. In very obstinate cases washing with ether was found advantageous; if, on the other hand, the extract was comparatively free from resin, it could be washed with alcohol upon a filter. In either case the residue was purified by recrystallization from alcohol until it showed the constant melting-point 178°.

The average yield of curcumin was 0.3 of one per cent: this, however, is only the amount that can be extracted by the process just described; the quantity contained in the root is much larger, as a considerable amount remained mixed with the resinous impurities, and the green fluorescence of the crude turmeric oil pointed to the presence of some curcumin in this substance.

Composition of Curcumin.

The following combustions were made of the curcumin purified as just described and dried at 100°. In most of these analyses a slight ash was left, the amount of which has been subtracted from the weight of substance before calculating the percentages.

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* Ber. d. ch. G. 1880, p. 338.

I. 0.1106 gr. of substance gave 0.2774 gr. of CO_2 and 0.0563 gr. of H_2O. No ash.

II. 0.2180 gr. gave 0.5450 gr. of CO_2 and 0.1099 gr. of H_2O. Ash 0.0007 gr.

III. 0.2149 gr. gave 0.5376 gr. of CO_2 and 0.1090 gr. of H_2O. Ash 0.0006 gr.

IV. 0.2195 gr. gave 0.5480 gr. of CO_2 and 0.1099 gr. of H_2O. Ash. 0.0006 gr.

V. 0.2743 gr. gave 0.6815 gr. of CO_2 and 0.1378 gr. of H_2O. Ash 0.0010 gr.

	I.	II.	III.	IV.	V.	Mean.
Carbon	68.43	68.39*	68.42*	68.27*	68.00*	68.30
Hydrogen	5.65	5.62	5.69	5.59	5.60	5.63

All these analyses were made with curcumin from Bengal turmeric: I. and II. of different portions of the same sample, III., IV., and V. of different samples.

The following analysis was made of curcumin extracted from Madras turmeric: —

0.3467 gr. gave 0.8612 gr. of CO_2 and 0.1870 gr. of H_2O. No ash.

Carbon	67.74
Hydrogen	5.99

The sample analysed was very red, and the somewhat lower percentage of carbon obtained was undoubtedly due to the presence of an impurity which causes the curcumin to crystallize in red burrs, as is shown by the following analysis of a very red sample of Bengal curcumin: —

0.2168 gr. of substance gave 0.5400 gr. of CO_2 and 0.1057 gr. of H_2O. No ash.

Carbon	67.93
Hydrogen	5.42

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* These numbers become, if the ash is not subtracted from the weight of the substance: —

	II.	III.	IV.	V.
Carbon	68.17	68.23	68.09	67.75
Hydrogen	5.60	5.64	5.56	5.58

It is to be observed, however, that enough of this impurity to change the crystalline habit and color of the curcumin has but a very slight effect on the percentage composition, and, it may be added, does not lower the melting-point more than one degree. That it is formed by the oxidation of curcumin by the action of the air, appears from the fact that pure yellow curcumin was partially converted into red burrs when moistened with alcohol and exposed to the air for a long time. When once formed, the impurity can be removed only by repeated crystallization, and the amount of Madras curcumin at our disposal did not admit of this, nor did we take the trouble to prepare a larger supply, as the above analysis with the melting-point 178° is sufficient to establish the identity of the Madras and Bengal curcumins.

The following comparison shows that our results agree tolerably well with those of Daube, but are entirely at variance with those of Kachler and Ivanow-Gajewsky. (As no analyses are given in the abstract of the latter's article, which alone is at our disposal, we have given the theory for his formula, $C_{16}H_{16}O_4$, under his name.)

	Ivanow-Gajewsky	Kachler		Daube			Jackson and Menke Mean
Carbon	70.58	69.90	69.87	67.90	67.89	67.92	68.30
Hydrogen	5.90	5.70	5.59	5.66	5.76	5.70	5.63

There are, then, eight analyses of curcumin, which support a percentage of carbon in the neighborhood of 68 against three (or more) in favor of one near 70.*

It is probable that the high results obtained by Ivanow-Gajewsky and Kachler were due to the presence of resinous impurities, since their predecessors, who analysed exceedingly impure curcumin, as shown by the low melting-point, obtained the following results.

	A. Vogel, Jr.	Bolley, Suida, and Lange
Carbon	69.50	69.07
Hydrogen	7.46	6.40

This view is further supported by the fact that we obtained a higher melting-point, 178°, than any one else; Daube found 165°, Ivanow-Gajewsky 172°, later 140°, while Kachler gives no melting-point, and did not succeed in obtaining his curcumin crystallized. In view of these facts we feel no hesitation in rejecting all the previous analytical results except those of Daube.

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* Ivanow-Gajewsky obtained a percentage of lead in a plumbic salt agreeing with his combustion; but this result is more than counterbalanced by the analyses of derivatives of curcumin given later in this paper.

Daube gives curcumin the formula $C_{10}H_{10}O_3$, but our results, and for that matter his, agree much better with the formula $C_{14}H_{14}O_4$, as appears from the following comparison: —

	$C_{10}H_{10}O_3$	$C_{14}H_{14}O_4$	Daube	Jackson & Menke
Carbon	67.42	68.29	67.90	68.30
Hydrogen	5.62	5.69	5.70	5.63

We have therefore adopted the formula $C_{14}H_{14}O_4$, which is also confirmed by the analyses of derivatives of curcumin to be given later in the paper.

Properties of Curcumin.

Curcumin crystallizes from alcohol in stout needles, which under the microscope appear as well-formed prisms with square ends, or spindle-shaped crystals, often arranged in radiating groups; in color it is orange to yellow, according to the size of the crystals, with a beautiful blue reflex; its solution in ether exhibits a very strong green fluorescence; when pure it has no odor; it melts at 178°, apparently with decomposition.* It is nearly insoluble in water, somewhat soluble in cold, more readily in hot alcohol and methyl alcohol, more soluble in glacial acetic acid than in alcohol, less so in ether, very slightly soluble in benzol † and carbonic disulphide, and essentially insoluble in ligroine. Strong sulphuric acid dissolves it with a fine reddish-purple color, which changes to black from charring after some time; strong hydrochloric acid produces the same effect, but with more difficulty. It is readily soluble in alkalies and alkaline carbonates, and is even dissolved to a slight extent when boiled with precipitated calcic carbonate and water. The solution in ammonic hydrate loses ammonia when boiled, and deposits unaltered curcumin. A solution of baric hydrate converts it into a blackish-red powder, but lime-water gives a red solution like that obtained from calcic carbonate. It is not affected by acid sodic sulphite.

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* Daube found 164°; Gajewsky, 172° or 140°.

† Compare Daube, Ber. d. ch. G. 1870, p. 609.

Salts of Curcumin.

In taking up the study of this subject we were at first attracted to the lead salt by the analyses and descriptions of Ivanow-Gajewsky and Daube; but, after several experiments, we decided that it was too indefinite a substance to throw much light upon the nature of curcumin, and accordingly turned our attention to the potassium salts, which at first did not seem promising, but on proper treatment have yielded satisfactory results. Before describing these, however, we will say, that there seem to be at least two lead salts, as we have obtained a dark claret precipitate and also a flame-colored one. The most promising method of preparation seemed to be boiling curcumin with precipitated calcic carbonate and water, and adding plumbic acetate to the filtrate; in this way the flame-colored salt was obtained.

We have succeeded in obtaining two potassium salts, containing one and two atoms of potassium respectively.

Dipotassic Salt of Curcumin $K_2C_{14}H_{12}O_4$.

This was made by adding a large excess of a strong alcoholic solution of potassic hydrate to a hot saturated solution of curcumin in alcohol; if the solutions are strong enough, flame-colored crystals of the salt are deposited on cooling; if this is not the case, it can be precipitated by addition of ether. If an insufficient amount of potassic hydrate is used, a dark red solution of the monopotassic salt is formed, which becomes lighter on the addition of more potassic hydrate as the second atom of potassium is taken up. The salt was crystallized from boiling alcohol to which a few drops of ether had been added, washed with a mixture of alcohol and ether, then with ether alone, pressed on filter-paper, and dried as rapidly as possible in a steam-drying closet containing some potassic hydrate.

0.7168 gr. of the salt gave, heated with sulphuric acid, 0.3824 gr. of K_2SO_4.

0.2675 gr. gave 0.1459 gr. of K_2SO_4.

	Calculated for $C_{14}H_{12}K_2O_4$	Found.	
Potassium	24.27	23.95	24.48

If curcumin had the formula $C_{16}H_{16}O_4$ the dipotassic salt would contain,

Potassium 22.46.

The salt consists when first formed of flame-colored needles in globular radiating groups, but becomes deep claret on drying. It is freely soluble in water, not quite so soluble in alcohol, and essentially insoluble in ether; the alcoholic solution takes on a magenta color when exposed to the air, and the salt seems to absorb carbonic dioxide readily, although the change of color was more probably due to oxidation.

Monopotassic Salt of Curcumin $KC_{14}H_{13}O_4$

If an excess of potassic carbonate is added to a hot solution of curcumin in absolute alcohol, there is a violent effervescence, and the liquid turns deep blood red. After slight concentration the excess of potassic carbonate was removed by filtration, the salt precipitated with ether, and purified by washing with ether. An attempt to crystallize it from a mixture of alcohol and ether gave no satisfactory result. Pressed between filter-paper, and then dried at 100°, it gave the following results: —

I. 0.4808 gr. of the salt gave after ignition with sulphuric acid 0.1540 gr. of K_2SO_4.

II. 0.5381 gr. of the salt gave 0.1680 gr. of K_2SO_4.

	Calculated for $KC_{14}H_{13}O_4$	Found.	
		I.	II.
Potassium	13.76	14.36	14.02

$KC_{16}H_{15}O_4$ contains 12.60 per cent of potassium.

The salt is precipitated in crimson black flocks, which dry to a mass having the green color and lustre of rosanilin, although the shade is somewhat blacker. It is very easily soluble in water and alcohol, giving blood-red solutions, but insoluble in ether, and does not seem to be altered by exposure to the air. It can also be made by the action of an excess of curcumin on the dipotassic salt, or by adding potassic hydrate not in excess to curcumin suspended in alcohol. It is very much more soluble than the dipotassic salt.

Curcumin forms also a flame-colored calcium salt, slightly soluble in water, which can be made by adding calcic chloride to a solution of the monopotassic salt. The same salt is formed in small quantity when calcic carbonate is boiled with curcumin and water or alcohol, carbonic dioxide being set free.

The zincic salt seems to be soluble, the baric salt insoluble,* while the silver salt is probably very unstable, as curcumin is decomposed when boiled for more than a minute with argentic nitrate and alcohol.

The fact that only one atom of the hydrogen contained in curcumin can be replaced by the potassium of potassic carbonate would point to the existence of one, and only one, carboxyl group in its molecule; the presence of this group is confirmed farther by the power of decomposing calcic carbonate possessed by curcumin.† The replacement of a second atom of hydrogen when curcumin is treated with potassic hydrate in excess indicates the existence of a hydroxyl group, probably a phenol hydroxyl, and it would seem, therefore, that curcumin is a diatomic monobasic acid.

Esters of Curcumin.

Although the analyses of the potassium salts had agreed with the formula of curcumin derived from the analysis of the original substance, it seemed desirable to confirm this formula still farther by the study of some derivative of curcumin more stable and easily handled than the salts; we accordingly took up the investigation of the esters, but found that the ethyl ester made by the action of ethyliodide on the dipotassic salt was a disagreeable brownish-black tarry substance, that could not be obtained in a crystalline condition. We therefore abandoned the study of this substance and turned our attention to the monoparabrombenzyl ester, which we preferred to the benzyl ester, in the first place because of the great tendency of the parabrombenzyl compounds to crystallize, and secondly, since the presence of bromine increased the difference between the percentages of carbon in the two formulas by more than five tenths of one per cent, and also gave a third element whose quantity could be determined.

Monoparabrombenzyl Ester of Curcumin $C_{14}H_{13}(C_7H_6Br)O_4$.

To an alcoholic solution of the monopotassic salt of curcumin an excess of parabrombenzylbromide was added, and the mixture allowed to stand for several days, when it was found that pale yellow crystals mixed with potassic bromide had been deposited; the dark-colored liquid was poured off, and the solid residue freed from parabrombenzylbromide by repeated treatment with hot ligroine, and from curcumin by boiling with successive portions of aqueous potassic carbonate, until it ceased to give a red solution. The essentially pure ester thus obtained was boiled several times with alcohol, which dissolved a small portion of it, while the residue melted to a reddish-black tar; upon dissolving this in glacial acetic acid and precipitating with water, yellowish flocks were thrown down, the melting-point of which was compared with that of the similarly-colored indistinct crystals obtained by cooling the alcoholic extract. As both these substances melted, or, more accurately, drew together, at the same temperature, the ester seemed to be essentially pure, and after drying at 50°–60° was analysed.

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* As our work on the potassium salts had achieved the end for which we undertook the study of the salts of curcumin, we thought it not worth while to purify any of the other salts for analysis.

† Some experiments on the action of phosphorous trichloride upon monoethylcurcumin confirmed the presence of a carboxyl group, as far as they went, but the product was too ill-defined to repay a thorough study.

I. 0.1796 gr. of substance gave 0.3980 gr. of CO_2 and 0.0817 gr. of H_2O.

II. 0.2506 gr. of substance gave according to Carius 0.1156 gr. of AgBr.

	Found.	Calculated for	
		$C_{14}H_{13}(C_7H_6Br)O_4$	$C_{16}H_{15}(C_7H_6Br)O_4$
Carbon	60.43	60.72	62.58
Hydrogen	5.05	4.57	4.76
Bromine	19.63	19.26	18.14

From these results there can be no doubt that $C_{14}H_{14}O_4$ is the true formula of curcumin.

The ester consists of indistinct crystals, grouped in forms like cauliflowers, of a much paler yellow color than curcumin; it melts at 76°–78°, beginning to draw together at 76°, and becoming thoroughly liquid at 78°; we have not succeeded in obtaining it with a perfectly sharp melting-point. It is more soluble in glacial acetic acid than in alcohol, nevertheless the latter is to be preferred as a solvent for obtaining crystals, since the substance is apt to separate from the hot glacial acetic acid in a fused tarry condition. It is readily soluble in ether and benzol, but does not crystallize well from these solvents; slightly soluble in carbonic disulphide; essentially insoluble in ligroine; not attacked by a solution of potassic carbonate, but soluble in potassic hydrate, although without the red color characteristic of curcumin. As the analysis of this ester establishes our formula, we have not continued the study of the esters.

Oxidation of Curcumin.

Our experiments on this subject can be divided into two classes, those in which we made a complete oxidation of the substance, and those in which a partial oxidation was obtained by using an insufficient amount of the oxidizing agent, or one less energetic.

Complete Oxidation. — As Ivanow-Gajewsky states that he obtained terephthalic acid by the action of potassic dichromate and sulphuric acid on curcumin, we turned our attention first to this experiment. Unfortunately only an abstract of his paper is accessible to us, so that we could not find the exact conditions of his oxidation; we have therefore varied the conditions in several ways, but always with the same result. It will be sufficient to describe a single experiment. Half a gramme of curcumin was mixed with sulphuric acid previously diluted with its own volume of water, and solid potassic dichromate added; the action was extremely violent, accompanied by great evolution of heat and strong effervescence; the gas given off was carbonic dioxide. At the end of the process there was no insoluble substance in the liquid, which was therefore distilled until it was reduced to a small volume. The strongly acid distillate, treated with argentic oxide, after filtering and concentration deposited long flattened needles, which looked exactly like argentic acetate, and were proved to consist of this substance by the following silver determination: —

0.1812 gr. of salt dried at 100° gave 0.1559 gr. of AgCl.

	Calculated for $AgC_2H_3O_2$	Found.
Silver	64.68	64.76

There was no other volatile acid in the distillate, and no organic matter could be found in residue from the distillation. If the action was moderated by using more dilute sulphuric acid, the phenomena were the same, except that it was necessary to start the reaction by the aid of heat. In none of the products of the oxidation of curcumin with potassic dichromate could any terephthalic acid be found, they consisted only of acetic acid and carbonic dioxide.

If curcumin is dropped into fuming nitric acid it dissolves with a hissing noise and formation of nitrous fumes and hydrocyanic acid. The red liquid thus obtained gave no precipitate with water; on evaporation it deposited brownish crystals, principally oxalic acid, but it was not further examined. In this respect we confirm the results of Daube, who also obtained oxalic acid from curcumin and nitric acid.

Incomplete Oxidation. — When curcumin was dissolved in aqueous potassic hydrate, a solution of potassic permanganate added, not in excess, and after the oxidation had ceased, the liquid acidified with sulphuric acid, a strong smell of vanilla was observed. The liquid was accordingly filtered, and the precipitate thoroughly washed with boiling water, the filtrate and wash-water extracted with ether, and the extract treated with acid sodic sulphite, as directed by Tiemann and Haarmann.* The product was an oil, having a strong smell of vanilla and gradually solidifying in circular groups of radiating needles; the amount, however, was extremely small, and none of this product was obtained with an excess of potassic permanganate or when the quantity of curcumin was much more than half a gramme. The same substance was obtained with various weak oxidizing agents, such as bleaching powder and water, potassic ferricyanide with potassic hydrate, and even the action of atmospheric oxygen on curcumin dissolved in potassic hydrate. Of these the mixture of potassic hydrate and potassic ferricyanide gave the best yield, but even this was extremely small, — in fact after uniting the product from all the oxidations made by us, in which over eight grammes of curcumin were used, the quantity was not enough for complete purification. By sublimation, however, and subsequent crystallization from boiling water, it was obtained in white needles resembling in appearance and odor the vanillin from the vanilla-bean and melting at 79°. Vanillin melts at 80°–81°.

In addition to the vanillin there were formed carbonic dioxide, a black amorphous substance with feebly acid properties, perhaps the aldehyd resin of vanillin, as it appeared in largest quantity when no vanillin was obtained, and an acid volatile with steam. We have not as yet made any complete study of these secondary products, because the properties of the humus-like substance are far from inviting, and the amount of the volatile acid is so minute that its isolation in quantity sufficient for analysis would be extremely laborious. We shall, however, return to these substances if we fail in finding easier methods for studying the nature of the side-chain.

As the small yield of vanillin was undoubtedly due to the presence of the phenol hydroxyl, which offered a point of attack for the oxidizing mixture, we next tried to increase our yield by replacing the hydroxyl hydrogen with some radical which would protect it from oxidation, and in this way not only prove that the substance was really vanillin, but also that it was one of the principal products of the oxidation. For this purpose we first tried to make acetylcurcumin by treating curcumin with acetylchloride: this gave a deep bluish-green liquid, which on standing turned brown, and then yielded on addition of water a yellowish precipitate which could not be obtained in crystals, its solutions forming on evaporation a dark-colored varnish. With acetic anhydride no better results were obtained, and as there seemed no prospect of getting a good analysis of the substance, it was at once oxidized with potassic permanganate. The result was not essentially better than that obtained with pure curcumin, and we accordingly turned our attention to the oxidation of diethylcurcumin, which was made by boiling the dipotassic salt with absolute alcohol and a slight excess of ethyliodide for six hours in a flask with a return cooler. On distilling off part of the alcohol and allowing the rest to evaporate spontaneously, the compound is left as a most uninviting brownish-black tar, which when heated with sodic hydrate dissolves with a dark red color resembling that of the alkaline solution of curcumin. Upon treating this solution with potassic permanganate until it was decolorized, filtering from manganic hydrate, and acidifying with sulphuric acid, a yellowish precipitate was obtained, which after two crystallizations from boiling water with bone-black melted at 195°, the melting-point given by Wassermann * for ethylvanillic acid (Tiemann † gives 193°–194°).

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* Ber. d. ch. G. 1875, p. 1115.

The nature of the substance was still further confirmed by the following combustion: —

0.1216 gr. of substance gave 0.2714 gr. of CO_2 and 0.0707 gr. of H_2O.

Calculated for $C_{10}H_{12}O_4$		Found.
Carbon	61.22	60.87
Hydrogen	6.12	6.46

There can be no doubt, therefore, that the substance is ethylvanillic acid, and it was formed in such quantity that it must be considered one of the principal products of the reaction. If the potassic permanganate was not added in excess, and the liquid extracted with ether, crystals of ethylvanillin were obtained, which on sublimation formed an oil solidifying after a short time in large twinned crystals like those

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* Ann. Chem. Pharm. 179, p. 366.

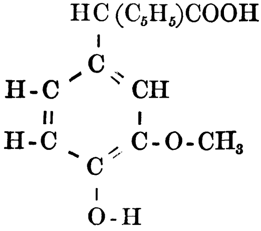
† Ber. d. ch. G. 1875. p 1127.

of cassiterite, and having a smell similar to that of vanillin, but not identical with it.

SUMMARY OF RESULTS.

The formula of curcumin is $C_{14}H_{14}O_4$, as proved by analyses of curcumin itself, of its potassium salts, and its parabrombenzyl ester.

It is a phenol-carboxylic acid, as shown by the study of its salts. The presence of carboxyl is indicated by its power of driving carbonic acid out of potassic and calcic carbonates, and by the decomposition of its diethylester on boiling with potassic hydrate. It contains the vanillin group, and therefore its formula, as far as we have determined it, is: —



We are at present engaged in the study of the group C_5H_5, and propose to extend our investigations to rosocyanin and the turmeric oil.